

Supporting Information

Cs₃W₃PO₁₃: A Tungsten Phosphate with One-dimensional Zigzag Tunnels Exhibiting Strongly Anisotropic Thermal Expansion

Pifu Gong,^{†§} Xingxing Jiang,^{†§} Yi Yang,^{†§} Siyang Luo,^{†} Rongjin Huang,[‡] Laifeng Li,[‡] Chuangtian Chen[†] and Zheshuai Lin^{*†§}*

[†] Beijing Center for Crystal Research and Development, Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[‡] State Key Laboratory of Technologies in Space Cryogenic Propellants, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[§] University of the Chinese Academy of Sciences, Beijing 100049, China.

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S1. Experimental Section

Single Crystal Growth

CsCO₃(AR, SCRC, China), WO₃(AR, SCRC, China), NH₄H₂PO₄(AR, XL, China) and B₂O₃(AR, SCRC, China) from commercial sources were used as raw materials. The single crystal of Cs₃W₃PO₁₃ was obtained by a flux method through spontaneous crystallization using B₂O₃ and WO₃ as the flux. The raw materials of CsCO₃, WO₃, NH₄H₂PO₄ and B₂O₃ were mixed in an agate mortar in the molar ratios 4: 3: 3: 3 and packed into a platinum crucible. The mixture was gradually heated to 973 K in a self-made furnace for 24h and additional B₂O₃ and WO₃ were added to adjust the viscosity and the volatility of the melt. After then the temperature was cooled down at a rate of 30 K per day until 800 K and finally quenched to room temperature. The products were place in water for 24h and many transparent, acicular crystals were obtained. The polycrystalline product can also be obtained by traditional high temperature solid-state reaction with a stoichiometric ratio of CsCO₃, WO₃ and NH₄H₂PO₄. The mixture were packed into a platinum crucible and heated to ~1000K over 5 days with several grindings. The powder samples were characterized by powder X-ray diffraction.

Single-Crystal Structure Determination

The single crystal X-ray diffraction measurements were performed on a Rigaku AFC10 diffractometer equipped with a graphite-monochromated K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The Crystalclear software was used for data extraction and integration and the program XPREP was used for face-indexed absorption corrections. The structures were solved by direct methods using SHELXS-97 and then refined by full-matrix least-squares refinement on F^2 with SHELXL-97¹ found in the software suite WinGX². The structures were verified using the ADDSYM algorithm from the program PLATON,³ and no higher symmetries were found.

X-ray Powder Diffraction

X-ray powder diffraction of the polycrystalline materials were performed at room temperature using an automated Bruker D8 Focus X-ray diffractometer equipped with

a diffracted monochromator set for Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. The scanning step width of 0.02° and the scanning rate of 0.2° s^{-1} were applied to record the patterns in the 2θ range of $10\text{--}75^\circ$.

Thermal Stability Measurement

About 10 mg of Cs₃W₃PO₁₃ were used for the DSC (LABSYS DSC thermal analyzer) measurement. The sample were placed in platinum crucibles and heated from room temperature to 850°C at the rate of $20^\circ\text{C}/\text{min}$ with surrounding N₂ gas. The melted residues were examined and analyzed by X-ray powder diffraction after the experiments.

Variable-temperature X-ray powder diffraction (VT-PXRD)

The variable-temperature X-ray powder diffraction was recorded on a Bruker D8-discover X-ray diffractometer equipped with a diffracted monochromator set for Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. Patterns at low temperature ($13\text{--}270 \text{ K}$) were separately recorded with a scanning step width of 0.01° . The low-temperature conditions were obtained using an G-M refrigerator, in which helium acts as the refrigerating fluid.

UV–Visible–Near-Infrared (NIR) Diffuse reflectance Spectroscopy

UV–visible–NIR diffuse reflectance data for the title compound were collected with a SolidSpec-3700 DUV spectrophotometer in the wavelength range from 300 to 1200 nm. Fluororesin was applied as the standard.

XPS Spectra measurement

The XPS spectra was collected with a PHI Quantera SXM X-ray photoelectron spectroscopy equipped with a hemispherical energy analyzer. The radii of the X-ray beam spot is 100 μm and step length of 0.1eV and the angle of incidence of 45° are chosen.

Computational Method

The first-principles calculations were performed using the plane-wave pseudopotential method implemented in the CASTEP package⁴. The local density approximation (LDA) with CA-PZ functionals and optimized norm-conserving pseudopotentials are adopted in these calculations. O $2s^22p^4$, P $3s^23p^5$, Cs $5s^25p^66s^1$

and W $5d^46s^2$ are treated as valence electrons. The kinetic energy cutoff of 900 eV and Monkhorst-Pack $1 \times 3 \times 1$ k-point meshes⁵ are used. The choice of these computational parameters is good enough to ensure the accuracy of present purpose.

Figure S1. X-ray powder diffraction patterns of $\text{Cs}_3\text{W}_3\text{PO}_{13}$. The bottom and middle panels show the simulated and measured XRD derived from the $\text{Cs}_3\text{W}_3\text{PO}_{13}$ crystal, respectively, while the top panel shows the XRD for the compound after melting.

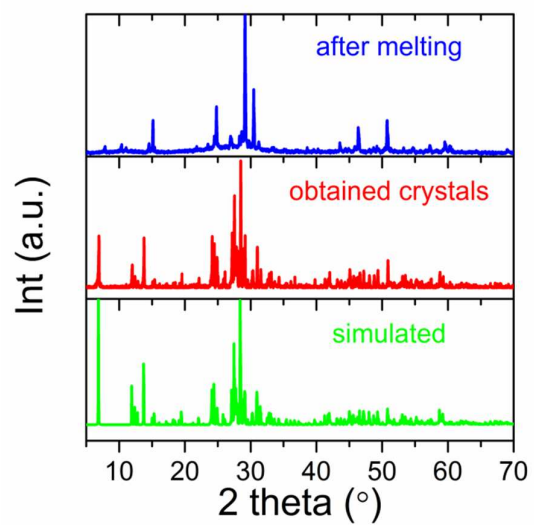


Figure S2. The local atomic environment of Cs atoms in $\text{Cs}_3\text{W}_3\text{PO}_{13}$.

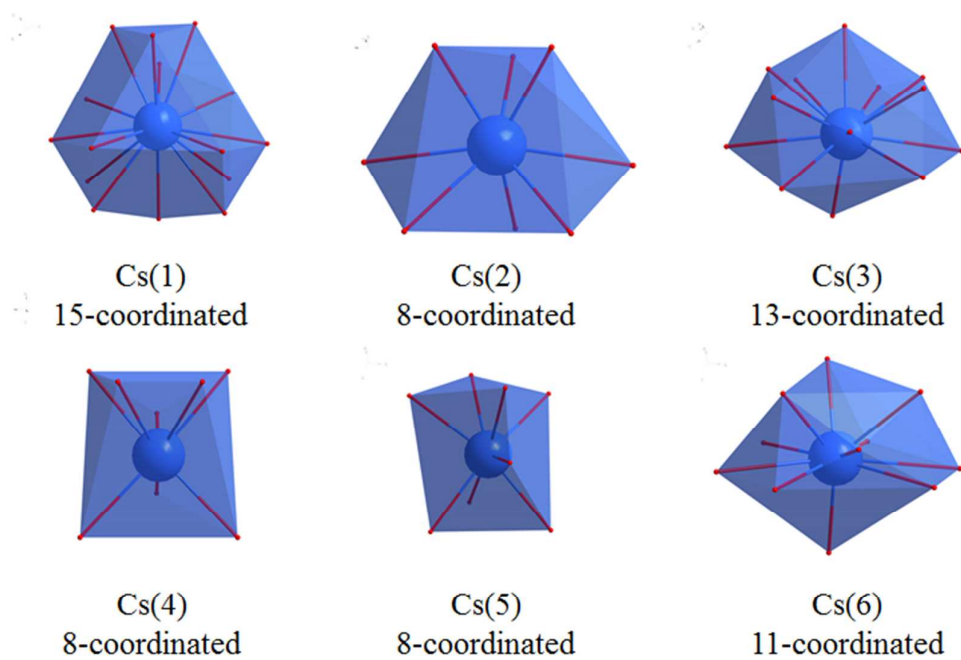


Figure S3. The electric band structure of $\text{Cs}_3\text{W}_3\text{PO}_{13}$ crystals, which show that $\text{Cs}_3\text{W}_3\text{PO}_{13}$ is a direct gap crystal with calculated band gap of 1.83 eV, which is smaller than its experimental value of 3.27 eV. The discrepancy between experimental and calculated band gap is due to the notorious issue of exchange-correlation functionals.⁶

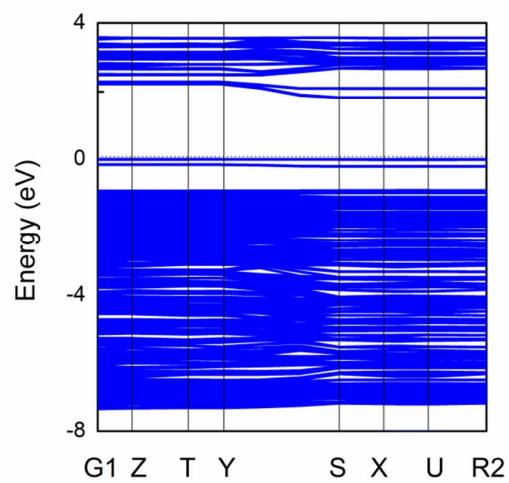


Figure S4. The XPS spectra of $\text{Cs}_3\text{W}_3\text{PO}_{13}$, whose binding energy is calibrated with $\text{C } 1s=284.8\text{eV}$. The main peaks of Cs 3d5 (located at 724.08 eV), O 1s (located at 529.08 eV), P 2p (located at 131.94 eV) and W 4f (located at 35.5 eV) can match with that of CsOH, Y_2O_3 , K_2HPO_4 and WO_3 , respectively, indicating the valence of +1, -2, +5 and +6 for cesium, oxygen, phosphorus and tungsten.⁷

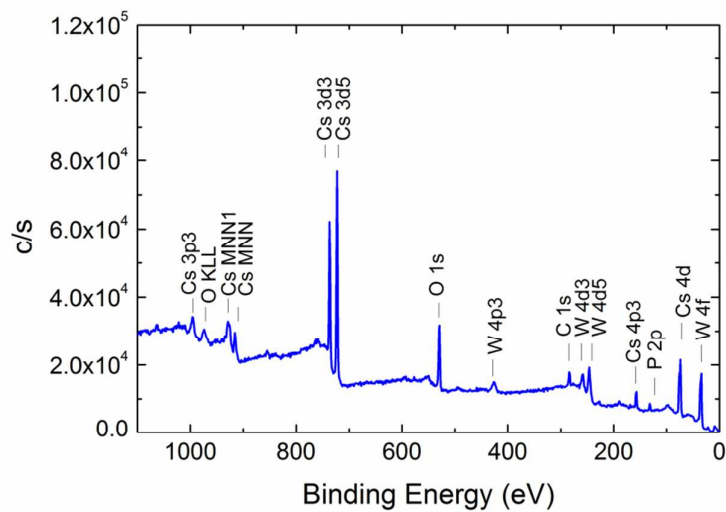


Table S1. Crystal data and structure refinements for Cs₃W₃PO₁₃

	Cs ₃ W ₃ PO ₁₃
Empirical formula	Cs ₆ O ₂₆ P ₂ W ₆
Formula weight	2378.38
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pnma
Unit cell dimensions	a = 14.9294(12) Å alpha = 90 deg. b = 7.1855(5) Å beta = 90 deg. c = 25.6895(19) Å gamma = 90 deg.
Volume	2755.8(4) Å ³
Z, Calculated density	4, 5.732 Mg/m ³
Absorption coefficient	32.969 mm ⁻¹
F(000)	4046
Crystal size	0.12 x 0.10 x 0.08 mm
Theta range for data collection	1.58 to 25.05 deg.
Limiting indices	-17 ≤ h ≤ 14, -8 ≤ k ≤ 8, -30 ≤ l ≤ 30
Reflections collected / unique	17125 / 2661 [R(int) = 0.553]
Completeness to theta = 25.05	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.1779 and 0.1098
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2661 / 289 / 211
Goodness-of-fit on F ²	1.109
Final R indices [I > 2σ(I)]	R1 = 0.0361, wR2 = 0.0827
R indices (all data)	R1 = 0.0400, wR2 = 0.0845
Largest diff. peak and hole	4.585 and -5.024 e.Å ⁻³
Empirical formula	Cs ₆ O ₂₆ P ₂ W ₆
Formula weight	2378.38
Temperature	293(2) K

Table S2. Atomic coordinates($\times 10^{-4}$) and isotropic displacement coefficients ($\text{\AA}^2 \times 10^{-3}$)
in $\text{Cs}_3\text{W}_3\text{PO}_{13}$.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
W(1)	8743(1)	2500	5770(1)	5(1)
W(2)	11119(1)	2500	6270(1)	5(1)
W(3)	9308(1)	-7(1)	7006(1)	6(1)
W(4)	7488(1)	-81(1)	4716(1)	5(1)
P(1)	6564(3)	2500	5658(2)	7(1)
P(2)	10254(4)	-2500	7935(2)	23(1)
O(1)	9536(9)	2500	7229(4)	10(2)
O(2)	8815(6)	711(10)	6384(3)	9(1)
O(3)	11567(6)	4285(10)	5687(3)	10(2)
O(4)	6622(6)	753(10)	5303(3)	9(2)
O(5)	7668(8)	2500	4601(4)	9(2)
O(6)	10576(6)	4398(10)	6587(3)	9(2)
O(7)	8481(6)	608(11)	5338(3)	9(1)
O(8)	6614(6)	-365(11)	4285(3)	14(2)
O(9)	9931(8)	2500	5731(4)	9(2)
O(10)	7439(8)	-2500	5041(4)	11(2)
O(11)	7409(8)	2500	6009(4)	11(2)
O(12)	10148(6)	-772(12)	7572(3)	16(2)
O(13)	8323(6)	-327(12)	7358(3)	17(2)
O(14)	9454(9)	-2500	6751(4)	11(2)
O(15)	12139(9)	2500	6590(5)	13(2)
O(16)	5710(10)	2500	5951(5)	21(3)
O(17)	9423(14)	-2500	8305(7)	51(4)
O(18)	11044(11)	-2500	8205(6)	29(2)
Cs(1)	5064(1)	7500	9416(1)	22(1)
Cs(2)	7275(1)	7500	8209(1)	52(1)
Cs(3)	12512(1)	-2500	8824(1)	19(1)
Cs(4)	5031(1)	7500	5559(1)	41(1)
Cs(5)	6649(1)	2500	7169(1)	30(1)
Cs(6)	9146(1)	2500	8385(1)	20(1)

Table S3. Atomic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) in $\text{Cs}_3\text{W}_3\text{PO}_{13}$.

	U3	U2	U3	U4	U5	U6
W(1)	8(1)	5(1)	1(1)	0	-1(1)	0
W(2)	9(1)	6(1)	1(1)	0	0(1)	0
W(3)	13(1)	3(1)	2(1)	1(1)	0(1)	0(1)
W(4)	10(1)	3(1)	3(1)	-1(1)	0(1)	0(1)
Cs(3)	24(1)	21(1)	13(1)	0	4(1)	0
P(1)	9(2)	9(2)	4(2)	0	0(2)	0
P(2)	27(1)	21(1)	21(1)	0	-2(1)	0
O(1)	16(4)	7(4)	8(4)	0	-3(4)	0
O(2)	13(3)	7(3)	8(3)	-1(2)	-1(3)	-1(2)
O(3)	13(4)	6(3)	10(3)	2(3)	0(3)	4(3)
O(4)	11(3)	7(3)	9(3)	-1(3)	2(3)	-1(3)
O(5)	16(4)	6(4)	6(4)	0	1(4)	0
O(6)	14(3)	4(3)	10(3)	-2(3)	-1(3)	-2(3)
O(7)	11(3)	9(3)	6(3)	3(2)	-1(3)	0(3)
O(8)	21(5)	10(4)	12(4)	-5(3)	-9(4)	3(3)
O(9)	9(2)	9(2)	8(2)	0	0(1)	0
O(10)	17(5)	7(4)	9(4)	0	2(4)	0
O(11)	11(2)	11(2)	11(2)	0	0(1)	0
O(12)	17(2)	16(2)	16(2)	0(1)	-1(1)	0(1)
O(13)	21(5)	16(4)	12(4)	4(3)	6(4)	-1(4)
O(14)	19(5)	7(4)	8(4)	0	0(4)	0
O(15)	13(3)	13(3)	13(3)	0	0(1)	0
O(16)	20(7)	25(6)	19(6)	0	5(5)	0
O(17)	51(4)	51(4)	51(4)	0	0(1)	0
O(18)	28(2)	30(2)	29(2)	0	-3(1)	0
Cs(1)	25(1)	23(1)	18(1)	0	-7(1)	0
Cs(2)	78(1)	30(1)	47(1)	0	41(1)	0
Cs(4)	25(1)	50(1)	47(1)	0	-3(1)	0
Cs(5)	27(1)	47(1)	17(1)	0	0(1)	0
Cs(6)	14(1)	39(1)	7(1)	0	1(1)	0

Table S4. Bond distances (Å) in $Cs_3W_3PO_{13}$.

bonds	length	bonds	length
W(1)-O(9)	1.776(12)	W(3)-O(12)	1.997(9)
W(1)-O(7)	1.797(8)	W(4)-O(8)	1.722(9)
W(1)-O(2)	2.038(8)	W(4)-O(5)	1.898(3)
W(1)-O(11)	2.085(12)	W(4)-O(10)	1.930(5)
W(2)-O(15)	1.731(13)	W(4)-O(4)	2.074(8)
W(2)-O(6)	1.783(8)	W(4)-O(7)	2.237(8)
W(2)-O(3)	2.082(8)	P(1)-O(16)	1.480(14)
W(2)-O(9)	2.250(12)	P(1)-O(11)	1.549(13)
W(3)-O(13)	1.742(9)	P(1)-O(4)	1.555(8)
W(3)-O(2)	1.835(8)	P(2)-O(18)	1.368(17)
W(3)-O(14)	1.919(4)	P(2)-O(12)	1.560(9)
W(3)-O(1)	1.920(4)	P(2)-O(17)	1.56(2)

Table S5. The angles for Cs₃W₃PO₁₃.

angle	degree	angle	degree
O(9)-W(1)-O(7)	100.5(3)	O(8)-W(4)-O(5)	97.1(5)
O(9)-W(1)-O(2)	89.5(4)	O(8)-W(4)-O(10)	98.2(4)
O(7)-W(1)-O(2)	90.7(3)	O(5)-W(4)-O(10)	162.4(5)
O(9)-W(1)-O(11)	166.1(5)	O(8)-W(4)-O(4)	91.7(4)
O(7)-W(1)-O(11)	88.5(3)	O(5)-W(4)-O(4)	85.4(4)
O(2)-W(1)-O(11)	79.7(3)	O(10)-W(4)-O(4)	85.5(4)
O(15)-W(2)-O(6)	100.5(4)	O(8)-W(4)-O(7)	171.0(4)
O(15)-W(2)-O(3)	93.4(4)	O(5)-W(4)-O(7)	78.5(4)
O(6)-W(2)-O(3)	90.2(3)	O(10)-W(4)-O(7)	85.1(4)
O(15)-W(2)-O(9)	170.4(5)	O(4)-W(4)-O(7)	80.2(3)
O(6)-W(2)-O(9)	85.6(3)	O(16)-P(1)-O(11)	113.9(7)
O(3)-W(2)-O(9)	79.1(3)	O(16)-P(1)-O(4)	110.3(5)
O(13)-W(3)-O(2)	98.7(4)	O(11)-P(1)-O(4)	107.2(4)
O(13)-W(3)-O(14)	98.6(5)	O(18)-P(2)-O(12)	113.0(5)
O(2)-W(3)-O(14)	90.6(4)	O(18)-P(2)-O(17)	112.1(10)
O(13)-W(3)-O(1)	96.8(5)	O(12)-P(2)-O(17)	106.4(6)
O(2)-W(3)-O(1)	93.8(4)	W(3)-O(2)-W(1)	150.8(5)
O(14)-W(3)-O(1)	163.1(5)	P(1)-O(4)-W(4)	134.0(5)
O(13)-W(3)-O(12)	96.7(4)	W(1)-O(7)-W(4)	138.8(4)
O(2)-W(3)-O(12)	164.6(4)	W(1)-O(9)-W(2)	138.8(6)
O(14)-W(3)-O(12)	85.4(4)	P(1)-O(11)-W(1)	127.3(7)
O(1)-W(3)-O(12)	86.0(4)	P(2)-O(12)-W(3)	135.8(6)

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